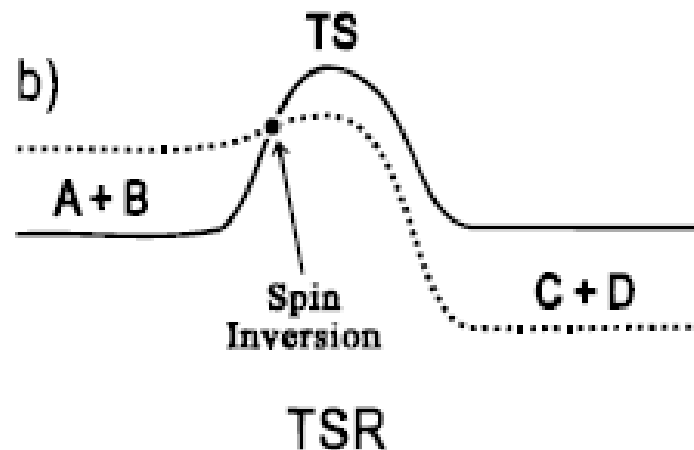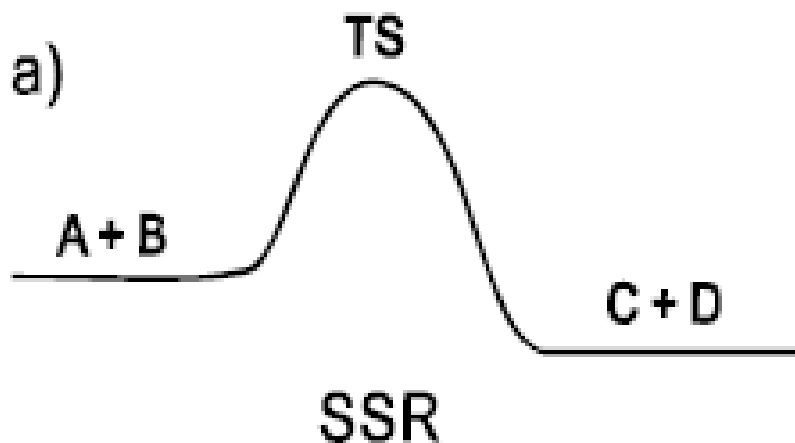# *Spin State in Organometallic Complex*
~Focusing on S. Shaik's work~

Literature Seminar
2013.4.15 H.Ikemoto (M1)

0. Introduction

It is proposed that spin-crossing effects can dramatically affect reaction mechanisms, rate constants, branching ratios, and temperature behaviors of organometallic transformations. This phenomenon is termed two-state reactivity (TSR) and involves par-

single-state reactivity (SSR)

0. Introduction

However... Such spin inversion had been dismissed as being unimportant, because of the lack of unambiguous experimental examples or computational method.

↓

After 1990, some groups have tackled this area.

0. Introduction

Prof. Sason Shaik

Sason Shaik received his B.Sc. and M.Sc. in chemistry from Bar-Ilan University and his Ph.D. from the University of Washington. He spent a postdoctoral year with Roald Hoffmann. In 1980, he started as a Lecturer at Ben-Gurion University, and in 1992 he moved to the Hebrew University, where he is currently the director of The Lise-Meitner-Minerva Center for Computational Quantum Chemistry. Among his awards is the 2007 Schrödinger Medal. His research interests range from bonding in small molecules to structure and reactivity of metalloenzymes.

Prof. Sason Shaik worked hard on changes of spin state of organometallic complex through reactions.

Today, I would like to introduce mainly Prof. Shaik's works.
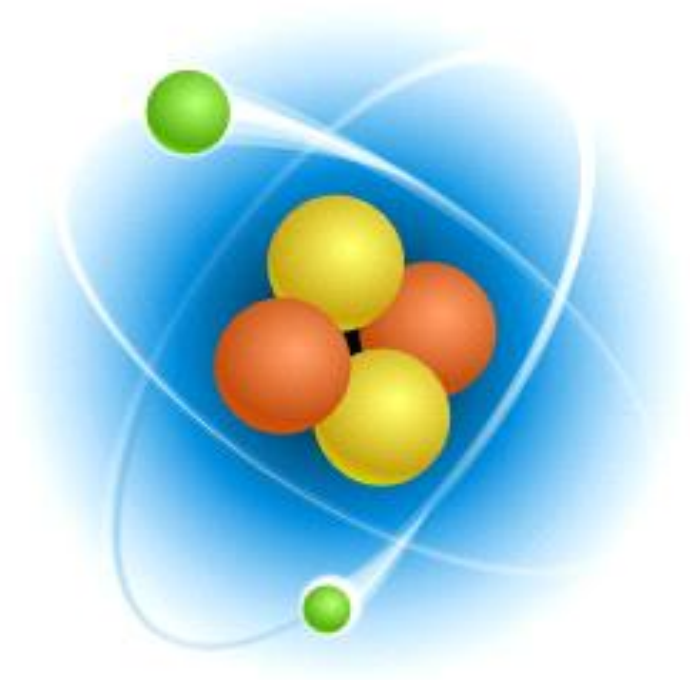
Today's Contents

0. Introduction

1. Spin Chemistry

2. Concept and Example of TSR

～Two-State Reactivity in Nonheme $Fe^{IV}=O$ Complex～

3. Summary and Perspective

1. Spin Chemistry

1. Spin Chemistry

The Selection rule (governing transitions of e⁻ between orbitals)

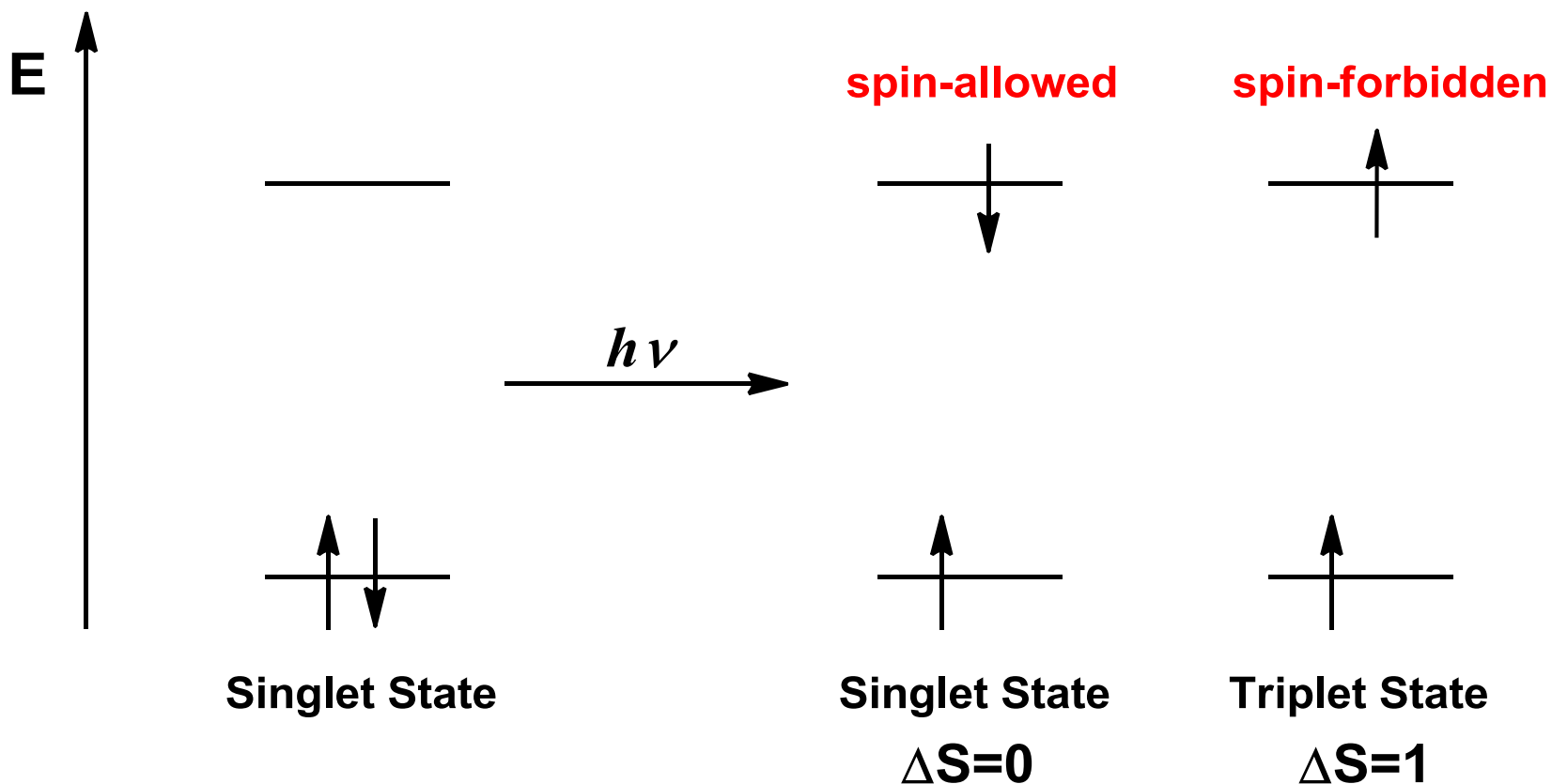In quantum mechanics, transition probability *P* is described like

$$P \propto \left| \int \psi_m \, r \, \psi_n \, d\tau \right|^2$$

↓

> 1. $\triangle S = 0$ (The Spin Rule)
> 2. $\triangle l = \pm 1$ (The Orbital Rule or Laporte Rule)

The first rule says that allowed transitions must involve the promotion of electrons without a change in their spin.
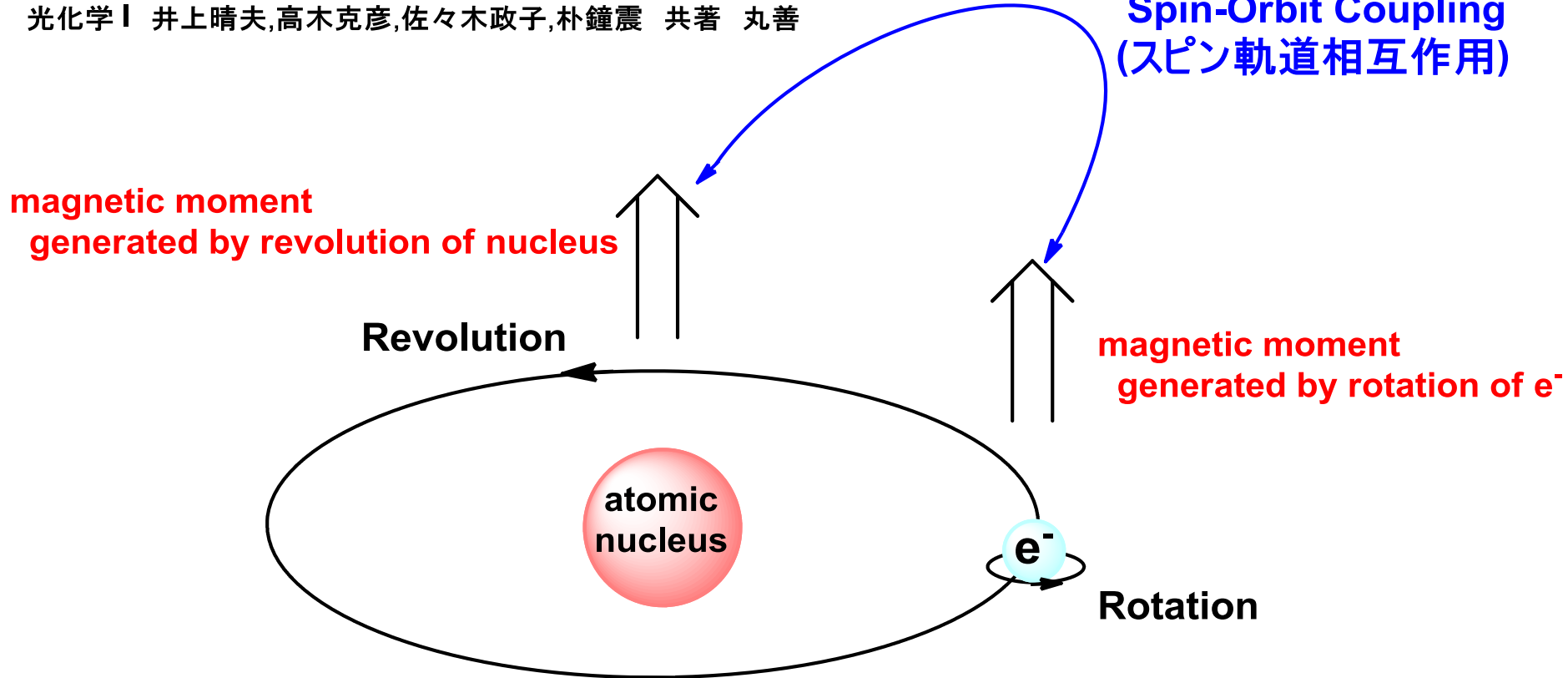
The second rule says that if the molecule has a centre of symmetry, transitions within a given set of p or d orbitals are forbidden.
(i.e. those which only involve a redistribution of electrons within a given subshell are forbidden)

1. $\triangle S=0$ (The Spin Rule)

E

spin-allowed　**spin-forbidden**

$h\nu$

Singlet State　　　**Singlet State**　　**Triplet State**

$\triangle S=0$　　　$\triangle S=1$

However, in some cases this rule is relaxed.

<u>Spin-Orbital</u> <u>Coupling</u> (<u>SOC</u>)

光化学 I 井上晴夫,高木克彦,佐々木政子,朴鐘震 共著 丸善

**Spin-Orbit Coupling
(スピン軌道相互作用)**

**magnetic moment
generated by revolution of nucleus**

Revolution

**magnetic moment
generated by rotation of e⁻**

**atomic
nucleus**

e⁻

Rotation

**If SOC is large, transition probability gets to be large.
Heavy atom has large nucleus, so SOC tends to be large.**

In heavy atom such as transition metal, spin inversion easily occur.

Heavy Atom Effect

Hund's rule

This rule predict that, in the ground state, atoms will have a maximum single occupancy in degenerate orbitals and therefore the highest possible spin quantum number.

Pauli exclusion principle

Spin-identical electrons avoid encounters, thus reducing repulsive interactions between electrons.

$\Longrightarrow$ *There are exchange interactions*

Exchange Interactions

K_{ij} : interactions between two electrons in the *i* orbital and *j* orbital

ex) atomic oxygen in the ground state is a triplet with two unpaired electrons in *2p* orbitals, K_{pp} = 25 kcal mol^{-1}

Exchange Interactions in Metals

Table 1 | Exchange interactions in transition metal cations and complexes

Atoms and diatomics	Sc	Ti	V	Cr	Mn	Fe	Co	Ni
$K_{dd'}$ (M$^+$)[a]	11.3	14.2	15.9	17.4	18.7	19.8	21.0	22.2
$K_{\pi^*\pi^*}$ (MO$^+$)				17.2[b]	17.7	13.6 (10.1[c])	11.4	13.2
	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd
$K_{dd'}$ (M$^+$)[a]	9.3	11.2	12.6	13.8	14.8	15.1	16.6	17.5
$K_{\pi^*\pi^*}$ (MO$^+$)					13.6	11.9	8.7	13.1
L_nFeO complexes[d]	1	2	3	4	5	6	7	8
$K_{\pi^*\pi^*}$	8.9 (9.5[e], 9.1[f])	9.1	8.8	12.0	9.1	9.3 (7.1[g])	12.0	12.0

Unless specified otherwise, *K* values (and orbital promotion gaps) are derived by B3LYP/def2-TZVP calculations using geometries optimized at the B3LYP/def2-TZVP level (for MO$^+$, FeO^{2+} and CrO) or published geometries (**1–8**)[9,15,43,44]. For details, consult the Supplementary Information. [a]Data are from ref. 31. These are state- and orbital-averaged values. [b]Value is for the neutral CrO species. [c]$K_{\pi^*\pi^*}$ value for FeO^{2+}. [d]**1**, (HS) Por$^{+\bullet}$Fe^{IV}=O [Por$^{+\bullet}$, porphyrin cation-radical]; **2**, [(NH$_3$)$_5$Fe^{IV}=O]$^{2+}$; **3**, [(HO)(NH$_3$)$_4$Fe^{IV}=O]$^+$; **4**, [(NH$_3$)$_4$Fe^{IV}=O]$^{2+}$; **5**, [N4PyFe^{IV}=O]$^{2+}$ [N4Py, N,N-bis(2-pyridylmethyl)N-bis(2-pyridyl)methylamine]; **6**, [(CH$_3$CN) TMCFe^{IV}=O]$^{2+}$ [TMC = 1,4,8,11-tetramethylcyclam]; **7**, [TMG$_3$trenFe^{IV}=O]$^{2+}$ [TMG$_3$tren = tris(2-(tetramethylguanidino)ethyl)amine]; **8**, TauD Fe^{IV}=O [TauD = taurin/α-ketoglutarate dioxygenase]. [e]This is an averaged value of two doublet excited states (with two π^* electrons being singlet coupled), from QM(CAS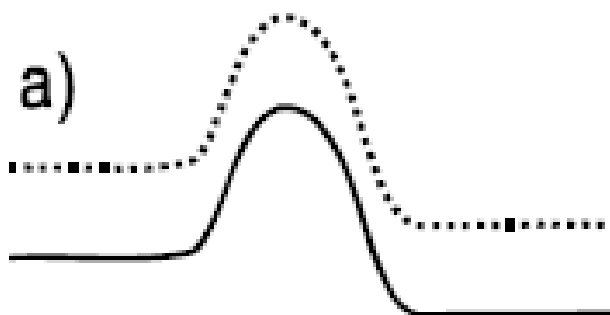PT2)/MM calculations[42] of **1** in P450cam. [f]A BP86 density functional value, based on published geometries[34]. [g]$K_{\pi^*\pi^*}$ value for [(CH$_3$CN)TMCRu^{IV}=O]$^{2+}$.

2. Concept and examples of TSR

~ Two-State Reactivity in Nonheme $Fe^{IV}=O$ Complex ~
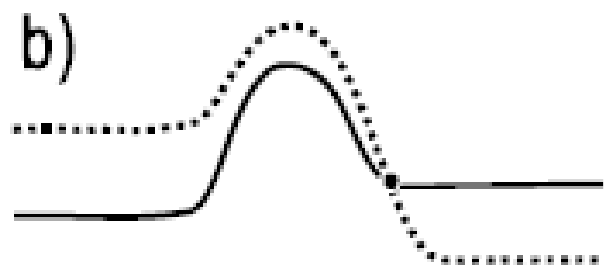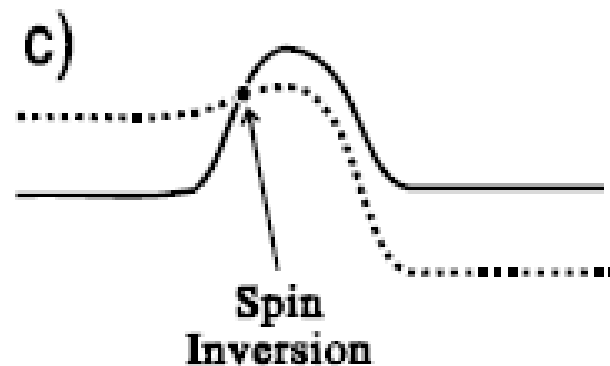
a)
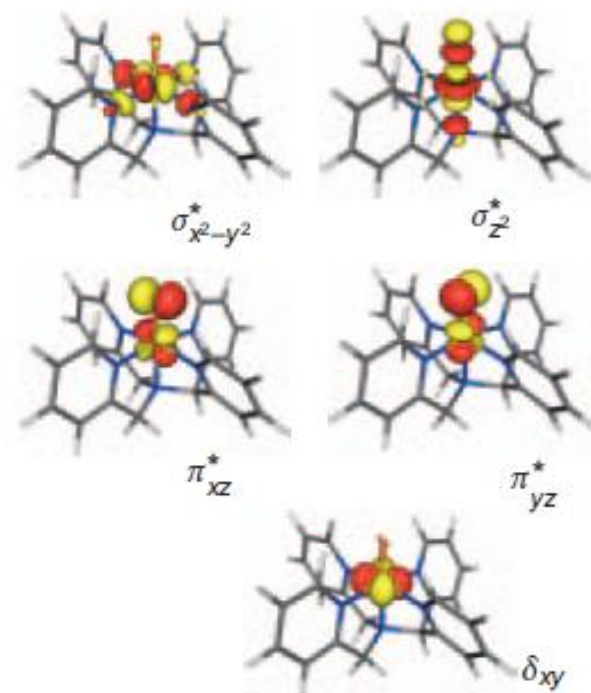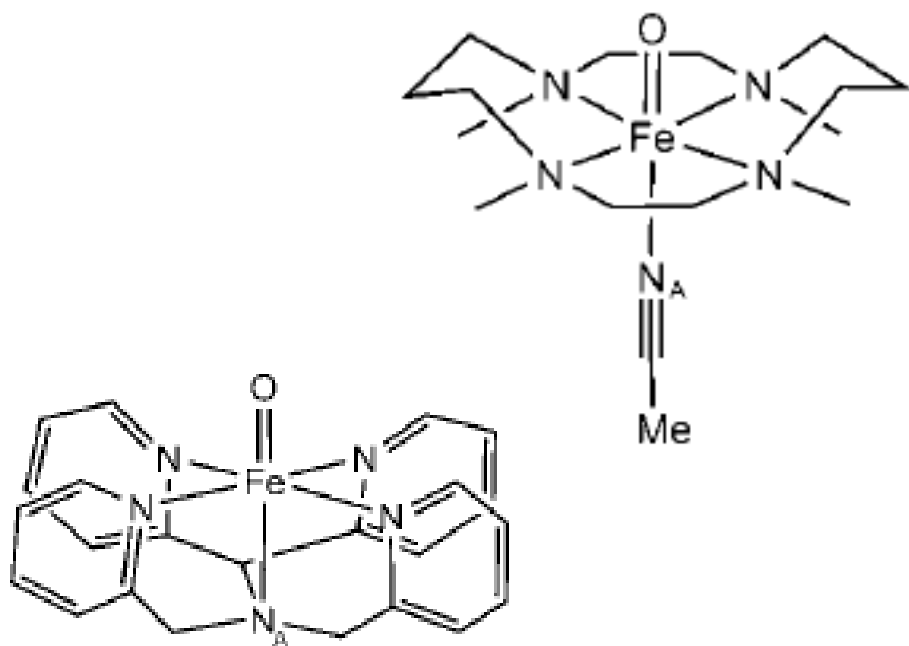
If the mechanisms and overall reaction enthalpies are similar on both surfaces, the Hammond postulate suggest that the excited surface remains above that of the ground state throughout the entire reaction.

$\longrightarrow$ **SSR**

b)

If the mechanisms are similar, but the reaction enthalpy of the excited surface is larger, crossing is likely to occur after passage of the TS.

$\longrightarrow$ **SSR**

c)

Spin
Inversion

If the mechanisms differ between two spin states, and TS energy of excited states(starting) is smaller, then crossing could occur along the reaction path.

$\longrightarrow$ **TSR**

Schröder, D., Shaik, S, Schwarz, H. *Acc. Chem. Res.* 2000, *33*, 139

Reactivity Change of Fe=O Complex

$[Fe^{IV}(O)(TMC)(X)]^{n+}$ (**1-X**) $[Fe^{IV}(O)(TMCS)]^+$ (**1'-SR**)
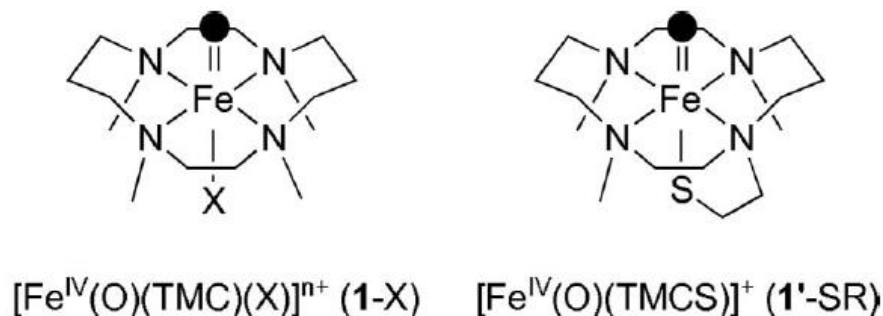
Fig. 1. Schematic structures of $[Fe^{IV}(O)(TMC)(X)]^{n+}$ (**1-X**) and $[Fe^{IV}(O)(T-MCS)]^+$ (**1'-SR**).
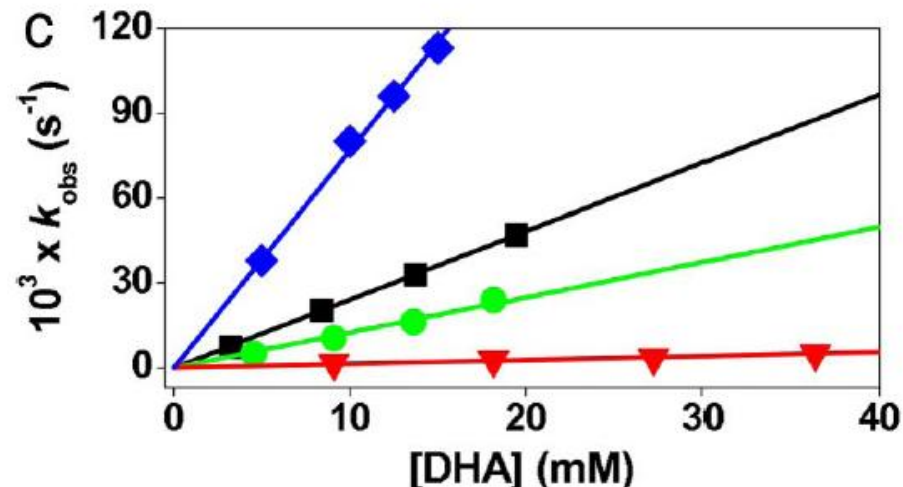
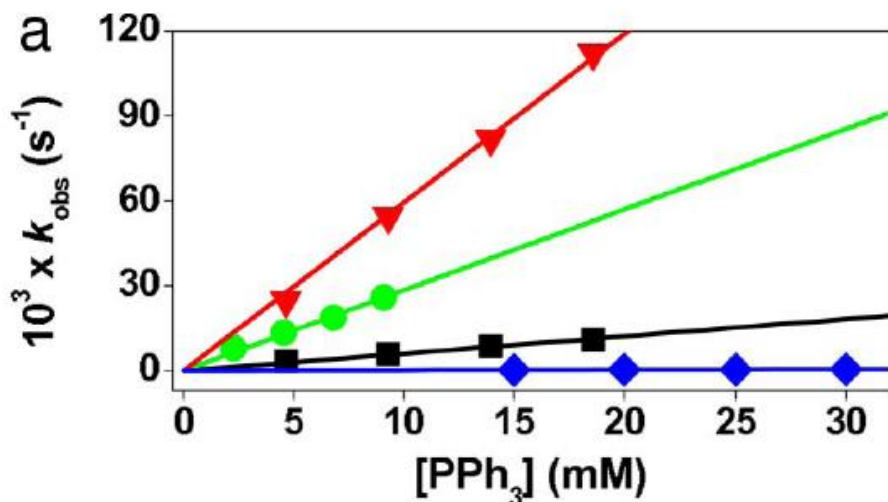**Fig. 2.** Second-order rate constants determined in the reactions of $[Fe^{IV}(O)(TMC)(X)]^{n+}$ (0.5 mM) at 0°C with PPh_3 (*a*), and DHA (*c*). Blue diamonds indicate **1'-SR**; black squares indicate **1-N_3**; green circles indicate **1-OOCCF_3**; and red inverted triangles indicate **1-NCCH_3**.

Property of Fe=O Complex

Shaik, S. *et al.* ACIE, 2008, 47, 3356

	2-NCCH$_3$	2-CF$_3$CO$_2$
r(Fe-O)	1.64 [1.64]	1.65 [1.65]
r(Fe-A)	2.12 [2.09]	1.97 [1.93]
Δq_{CT}	0.27 [0.27]	0.47 [0.49]
ΔE(Q–T)	6.9	5.0
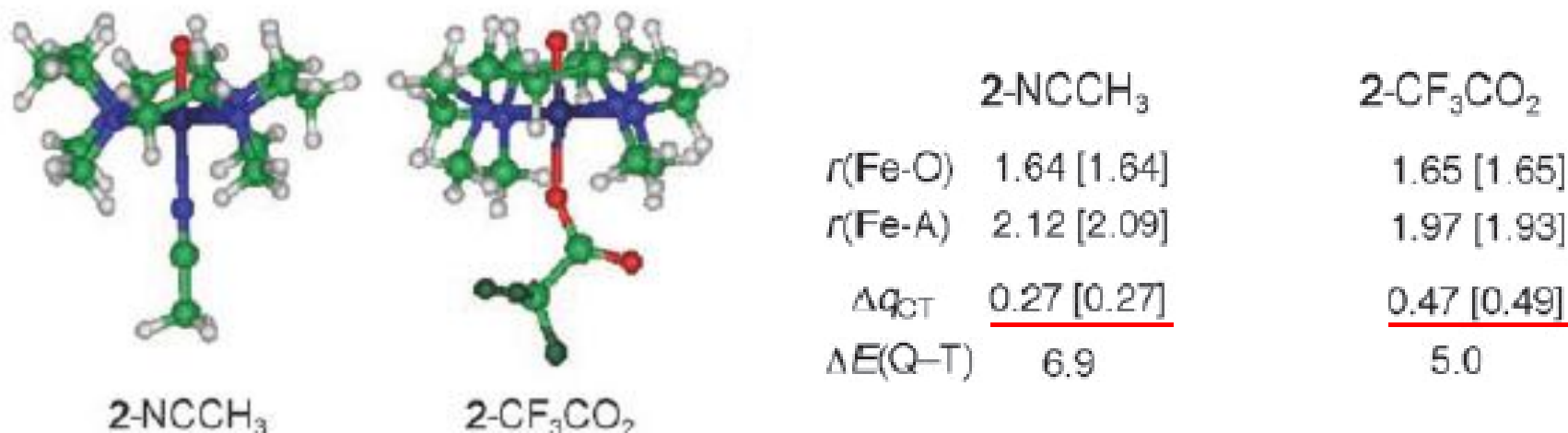
Figure 2. Key geometric features of the triplet [quintet] states of $[M^{IV}(O)(tmc)(X)]^{n+}$ complexes[6] obtained at the B3LYP/LACVP computational level; bond lengths are given in [Å]. "A" is the atom in the axial ligand coordinating to Ru or Fe. Also shown are the corresponding quintet–triplet energy gaps ΔE(Q-T) [kcal mol^{-1}] and the charge-transfer parameters Δq_{CT}.

More electron rich 2-CF$_3$CO$_2$ complex has less reactivity on the oxydation of PPh$_3$,but higher on DHA.

Comparison to Ru=O Complex

2-X

	2-NCCH$_3$	2-CF$_3$CO$_2$	2-N$_3$	2-Cl	2-NCO
r(Ru-O)	1.79 [1.79]	1.81 [1.80]	1.83 [1.82]	1.81 [1.81]	1.82 [1.82]
r(Ru-A)	2.26 [2.25]	2.11 [2.09]	2.10 [2.07]	2.50 [2.46]	2.08 [2.05]
Δq_{CT}	0.22 [0.23]	0.42 [0.44]	0.53 [0.56]	0.69 [0.75]	0.44 [0.44]
ΔE(Q–T)	46.8	45.2	43.2	42.8	43.4

1-X

	1-NCCH$_3$	1-CF$_3$CO$_2$	1-N$_3$
r(Fe-O)	1.64 [1.64]	1.65 [1.65]	1.67 [1.67]
r(Fe-A)	2.12 [2.09]	1.97 [1.93]	1.96 [1.94]
Δq_{CT}	0.27 [0.27]	0.47 [0.49]	0.57 [0.61]
ΔE(Q–T)	6.9	5.0	2.7
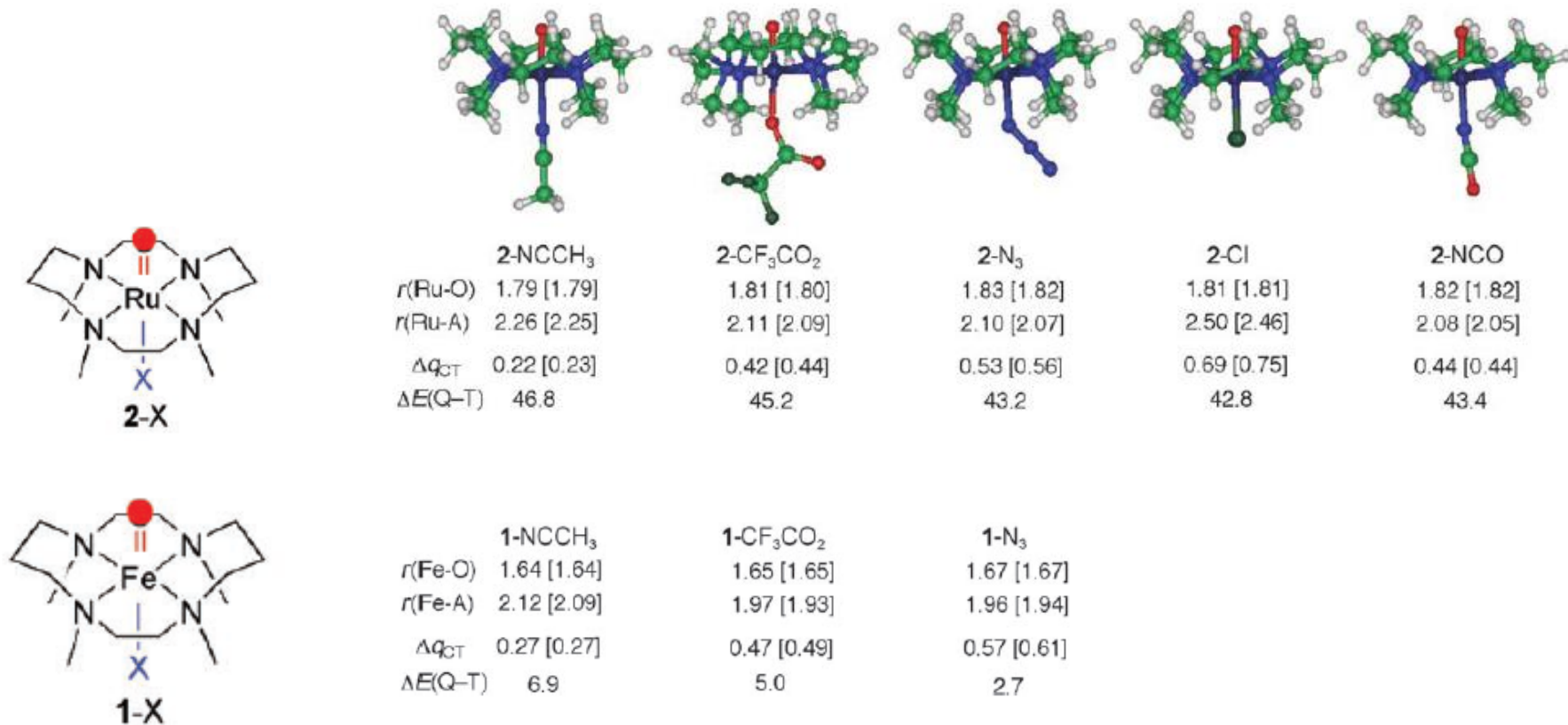
**Do Ru=O complexes show the same reactivities as Fe=O ??
If there are any differences, then how are they explained??**

d-Block Orbitals

Scheme 2. Electronic Configurations in the d-Block Orbitals of the Lowest Spin-States of $^{2S+1}K_L^Z$ Complexes; Orbital Drawings Were Made with *MOLEKEL*[39]

(a) triplet

(b) quintet (c) singlet

^3K_L

^5K_L ^1K_L

S = 1

S = 2   S = 0

$\sigma^*_{z^2}$

σ^*_{xy}

π^*_{xz} π^*_{yz}

δ

$^{2S+1}K_L$: 2S+1 indicates spin states, L indicates ligand.
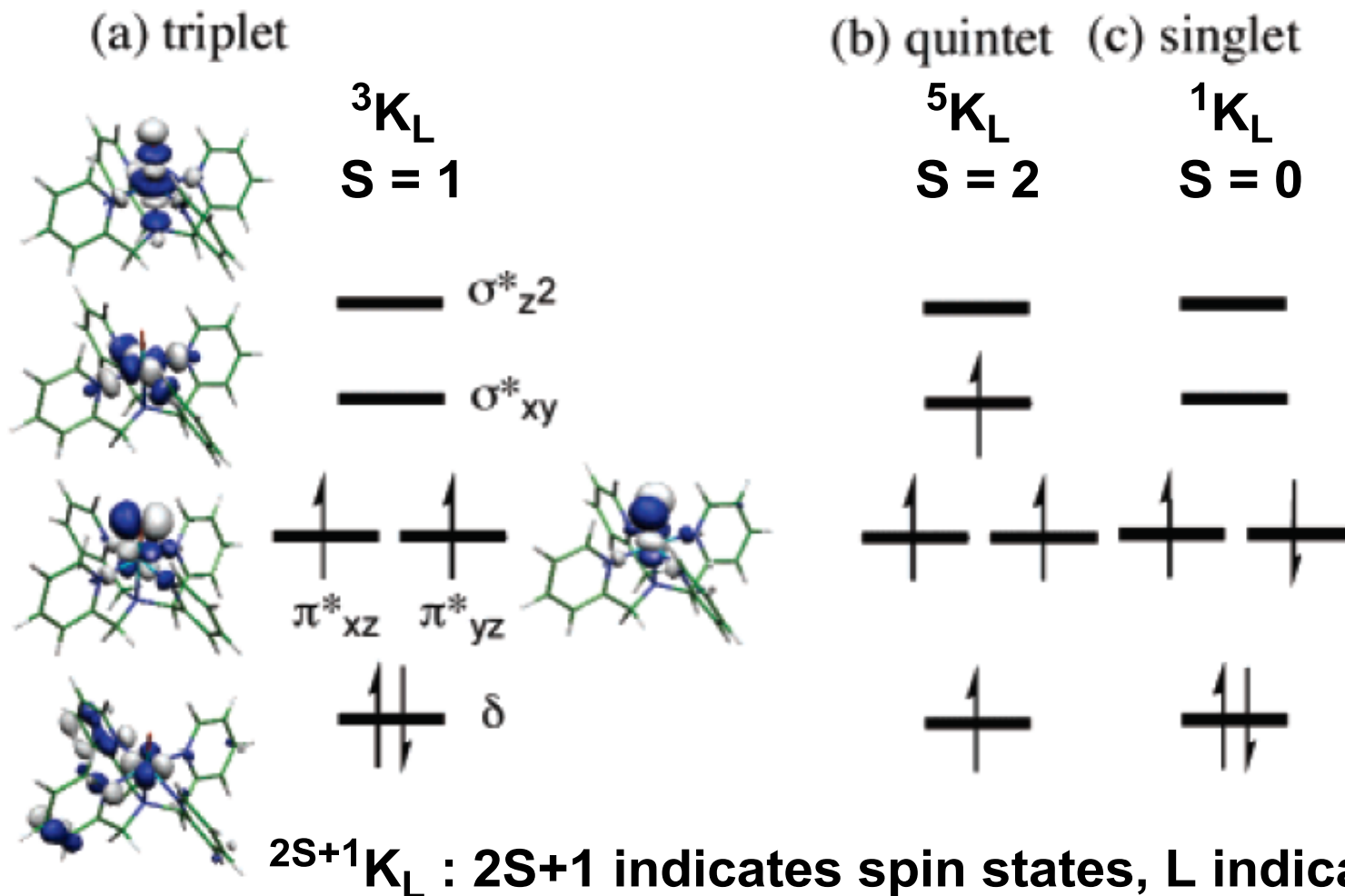
Example of Energy Profile

2. Concept and examples of TSR

Shaik, S. *et al. JACS*, **2006,** *128*, 8590.
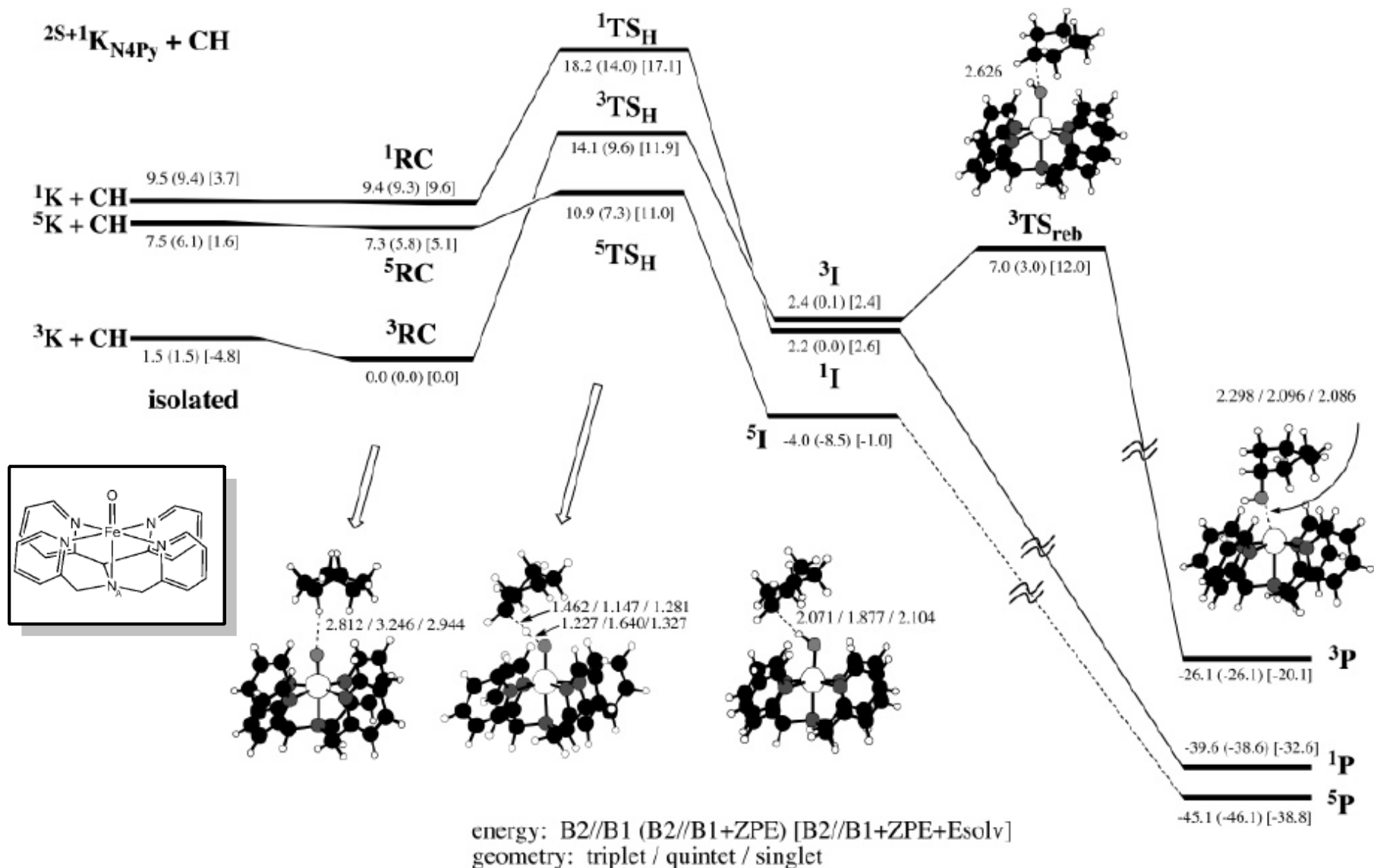
Figure 2. Energy profile for the reaction of $^{2S+1}K_{N4Py}$ ($S = 0, 1, 2$) with cyclohexane (**CH**). Relative energies are indicated in the order: B2//B1 (B2//B1 + ZPE) [B2//B1 + ZPE + E_{solv}]. Key bond lengths (in Å) are noted for the spin-state species, in the order: triplet/quintet/singlet.

energy: B2//B1 (B2//B1+ZPE) [B2//B1+ZPE+Esolv]
geometry: triplet / quintet / singlet

$^{2S+1}K_{N4Py}$ + CH

^1TS_H 18.2 (14.0) [17.1]

^3TS_H 14.1 (9.6) [11.9]

^1RC 9.4 (9.3) [9.6]

^1K + CH 9.5 (9.4) [3.7]

^5K + CH 7.5 (6.1) [1.6]

^5RC 7.3 (5.8) [5.1]

^5TS_H 10.9 (7.3) [11.0]

^3K + CH 1.5 (1.5) [-4.8]

^3RC 0.0 (0.0) [0.0]

isolated

^3I 2.4 (0.1) [2.4]

^1I 2.2 (0.0) [2.6]

^5I -4.0 (-8.5) [-1.0]

$^3TS_{reb}$ 7.0 (3.0) [12.0]

2.626

2.298 / 2.096 / 2.086

2.812 / 3.246 / 2.944

1.462 / 1.147 / 1.281
1.227 /1.640/1.327

2.071 / 1.877 / 2.104

^3P -26.1 (-26.1) [-20.1]

^1P -39.6 (-38.6) [-32.6]

^5P -45.1 (-46.1) [-38.8]

Feature of Energy Profile

- ^5TS_H is lower than ^3TS_H.

$$^3TS_H$$
14.1 (9.6) [11.9]

10.9 (7.3) [11.0]

$$^5TS_H$$

$$^3TS_{reb}$$
7.0 (3.0) [12.0]

$$^3I$$
2.4 (0.1) [2.4]

2.2 (0.0) [2.6]
$$^1I$$

$$^5I$$ -4.0 (-8.5) [-1.0]
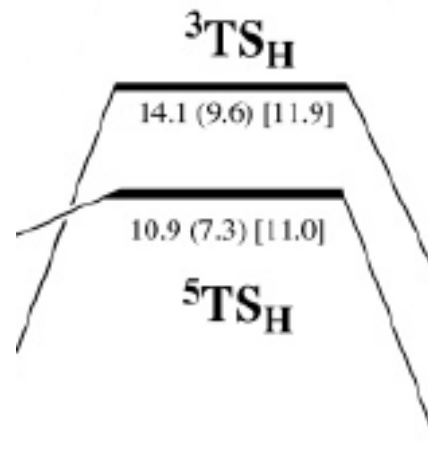
- **Only on the triplet surface, there is a barrier again.**

$$^3P$$
-26.1 (-26.1) [-20.1]

-39.6 (-38.6) [-32.6] $$^1P$$

$$^5P$$
-45.1 (-46.1) [-38.8]
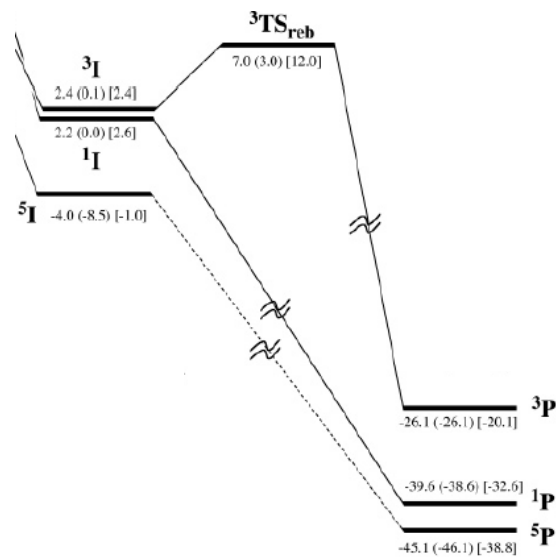
Orbital Occupancy-Evolution Diagrams help us to simplify and explain the features.

Scheme 3. Orbital Diagrams Showing the Evolution in d-Orbital Occupancy along the Oxidation Pathway; Both π and π^* Orbitals Involve Initially the Fe=O Moiety[46]

About ³TS_H state

The barrier is high in triplet state which loses one stabilizing exchange interaction.

About ^5TS_H state

In quintet state, four new exchange interaction are created, which leads to small barrier.
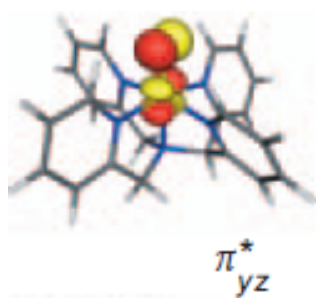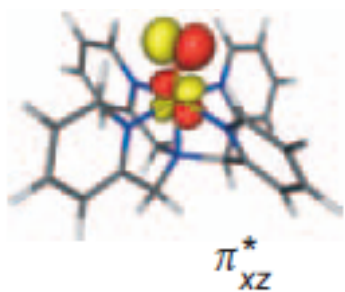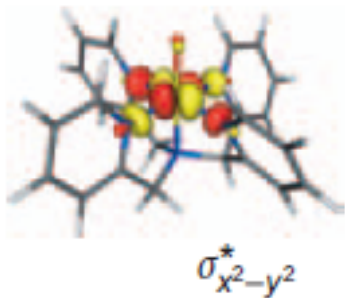
Quintet vs Triplet

^5TS_H

σ_{CH}

$\sigma^*_{Z^2}$

$\angle FeOH \sim 180°$

$\sigma^*_{Z^2}$

^3TS_H

σ_{CH}

π^*_{FeO}

$\angle FeOH \sim 120°$

π^*_{xz}

K_{N4Py} + TE

$Q_R = 0.37 \ [0.31]$

1.282 [1.135]
1.302 [1.770]

$\angle Fe\text{-}\overset{..}{O}\text{-}\overset{..}{H} = 143.2 \ [173.8]$
$\angle Fe\text{-}O\text{-}C = 148.9 \ [169.4]$
$\angle O\text{-}H\text{-}C = 167.8 \ [171.2]$

Each datum is given two numbers
corresponding to triplet [quintet], respectively.

The direction of d-orbital is also better in the quintet state.

Rebound Barrier

2. Concept and examples of TSR

Shaik, S. *et al. Nat. Chem.*, 2011, *3*, 19.
Shaik, S. *et al. JACS*, 2006, *128*, 8590.
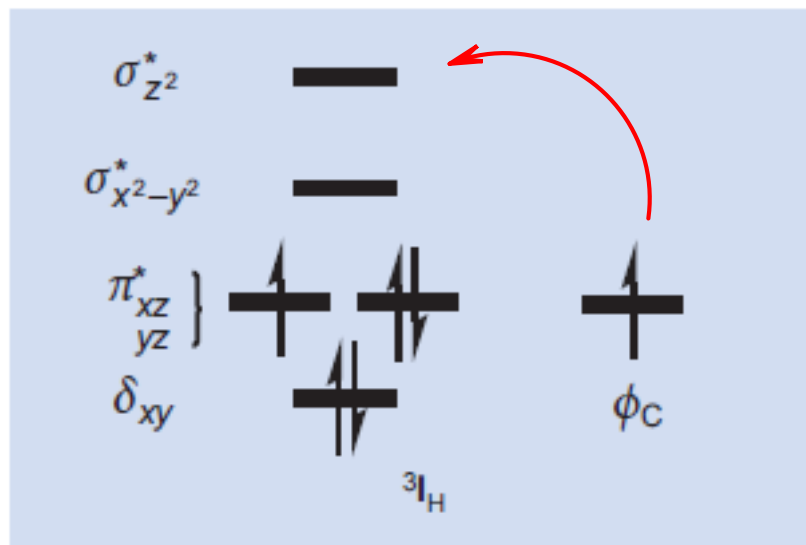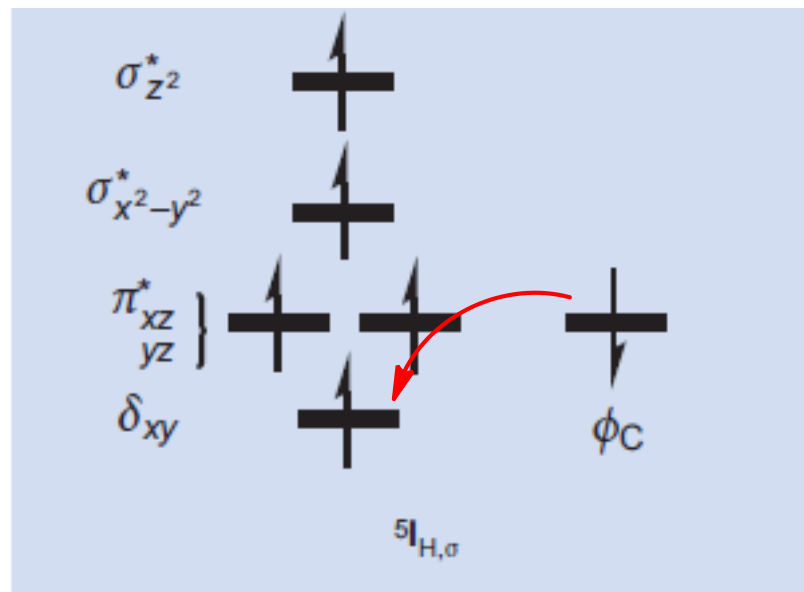
endothermal   **exothermic**

The triplet surface has rebound barrier.

In most cases, the quintet surface has no rebound barrier, or has small barrier.

Effect of Axial Ligands

1-X

PPh$_3$: 1-NCCH$_3$ > 1-O$_2$CCF$_3$ > 1-N$_3$ > 1-SR

C-H abstarction: **1-NCCH$_3$ < 1-O$_2$CCF$_3$ < 1-N$_3$ < 1-SR**

Table 1. Second-order rate constants and KIE values determined in substrate oxidations by [Fe^{IV}(O)(TMC)(X)]$^{n+}$ (1-X) and [Fe^{IV}(O)(TMCS)]$^+$ (1'-SR)

Substrate	k_2, M^{-1}·s^{-1}			
	1-NCCH$_3$	1-OOCCF$_3$	1-N$_3$	1'-SR
PPh$_3$	5.9	2.9	0.61	[0.016]
2,4-t-Bu$_2$C$_6$H$_3$OH	0.050	0.63	4.3	[12]
Xanthene	0.39	7.6	9.6	

Rate constants were determined at 0°C in CH$_3$CN for 1-X or 1:1 CH$_3$CN/MeOH for 1'-SR. Square brackets designate values obtained in 1:1 CH$_3$CN/CH$_3$OH at 0°C. The spectral changes were monitored at 820 nm for 1-NCCH$_3$, 835 nm for 1-OOCCF$_3$ and 850 nm for 1-N$_3$ and 1'-SR. Rate constants are averaged by three determinations, and standard deviation is <10% of the given values. N/A, not applicable.

Effect of Axial Ligands

	1-NCCH$_3$	1-OOCCF$_3$	1-N$_3$	1'-SR
r(Fe-O)	1.64 (1.64)	1.65 (1.65)	1.67 (1.67)	1.68 (1.68)
r(Fe-A)	2.12 (2.09)	1.97 (1.93)	1.96 (1.94)	2.37 (2.36)
Δq_{CT}	0.27 (0.27)	0.47 (0.49)	0.57 (0.61)	0.88 (0.95)
ΔE(Q–T)	6.9	5.0	2.7	0.2

Fig. 5.   Key geometric features of 1-NCCH$_3$, 1-OOCCF$_3$, 1-N$_3$, and 1'-SR optimized at the B3LYP/LACVP level (bond lengths in angstroms) in the triplet (quintet) states, along with the amounts of charge shifted from ligand to the (TMC)FeO moiety (Δq_{CT}) and the quintet–triplet energy gap (ΔE_{Q-T}, in kcal/mol).

$$\Delta q_{ct} : \text{1-NCCH}_3 < \text{1-O}_2\text{CCF}_3 < \text{1-N}_3 < \text{1-SR}$$

Effect of Axial Ligands

2. Concept and examples of TSR

Shaik, S. *et al.* PNAS, 2007, *104*, 19181.
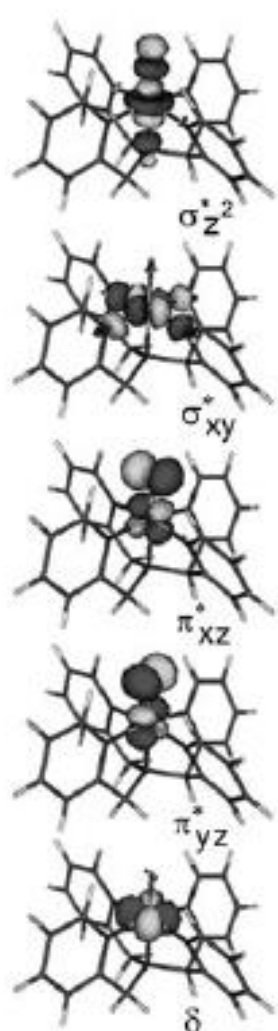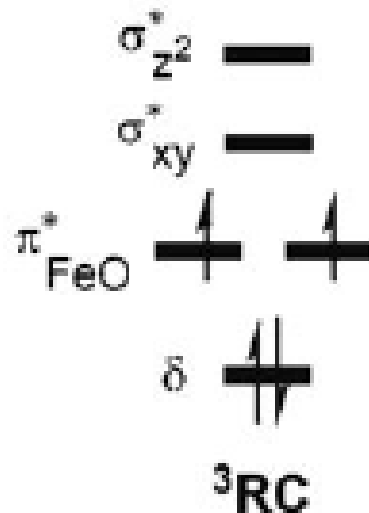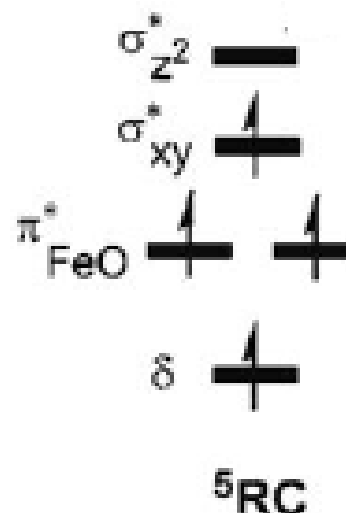
The stronger electron-electron repulsion of the axial ligand with the electron pair in δ orbital of Fe, the easier it would be to excite an electron to the σ^*_{xy} orbirtal and stabilize the quintet state.

$\longrightarrow$ *TSR is likely to occur.*

Defference between Fe^{IV}=O and Ru^{IV}=O

Shaik, S. *et al. ACIE*, 2008, *47*, 3356.

1-X

PPh$_3$: 1-NCCH$_3$ > 1-O$_2$CCF$_3$ > 1-N$_3$ > 1-SR

toluene: 1-NCCH$_3$ < 1-O$_2$CCF$_3$ < 1-N$_3$ < 1-SR

(Because oxidations occur with TSR.)

2-X
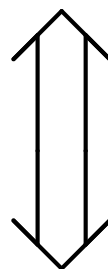
PPh$_3$: 2-NCCH$_3$ > 2-O$_2$CCF$_3$ > 2-N$_3$ > 2-SR

toluene: 2-NCCH$_3$ > 2-O$_2$CCF$_3$ > 2-N$_3$ > 2-SR

Reactivity follows electrophilicity of 2-X.

Oxidation by Ru^{IV}=O and its property

Spectral changes of reaction
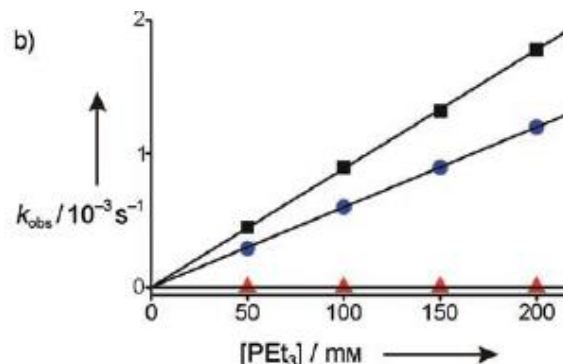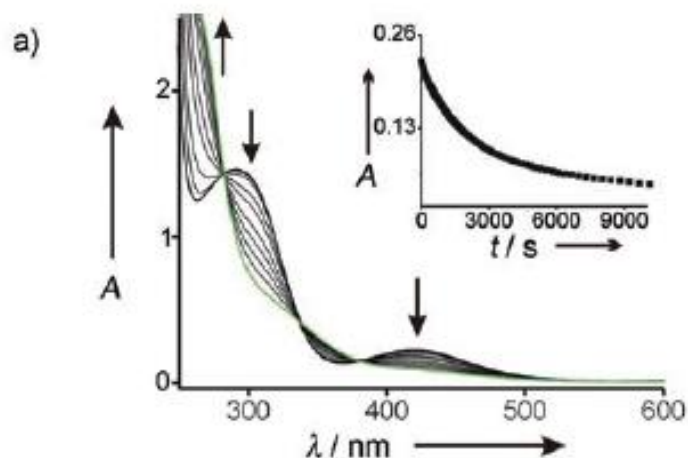
Figure 3. Reactions of 2-X with PEt$_3$ and xanthene. a) UV/Vis spectral changes of 2-NCCH$_3$ (1 mM) on addition of PEt$_3$ (50 mM) in CH$_3$CN at 35°C. The inset shows the time course of the decay of 2-NCCH$_3$ monitored at 420 nm. b) Plot of k_{obs} against PEt$_3$ concentration to determine second-order rate constants in CH$_3$CN at 35°C. Black squares: 2-NCCH$_3$; blue circles: 2-CF$_3$CO$_2$; red triangles: 2-Cl, 2-NCO, 2-N$_3$, and 2-NCS. c) Plot of k_{obs} against xanthene concentration to determine second-order rate constants in CH$_3$CN at 35°C. Black squares: 2-NCCH$_3$; blue circles: 2-CF$_3$CO$_2$; red triangles: 2-Cl, 2-NCO, 2-N$_3$, and 2-NCS.
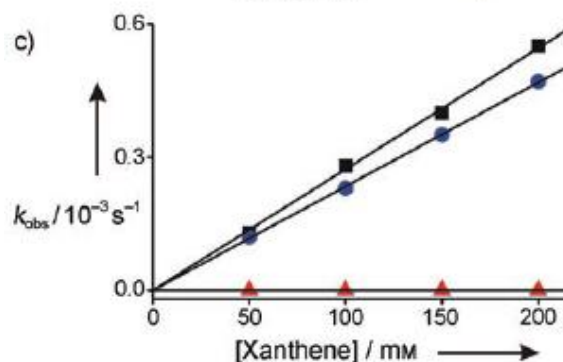
Computational analysis

	2-NCCH$_3$	2-CF$_3$CO$_2$	2-N$_3$	2-Cl	2-NCO
r(Ru-O)	1.79 [1.79]	1.81 [1.80]	1.83 [1.82]	1.81 [1.81]	1.82 [1.82]
r(Ru-A)	2.26 [2.25]	2.11 [2.09]	2.10 [2.07]	2.50 [2.46]	2.08 [2.05]
Δq_{CT}	0.22 [0.23]	0.42 [0.44]	0.53 [0.56]	0.69 [0.75]	0.44 [0.44]
ΔE(Q–T)	46.8	45.2	43.2	42.8	43.4

Reactivity order of Ru^{IV}=O

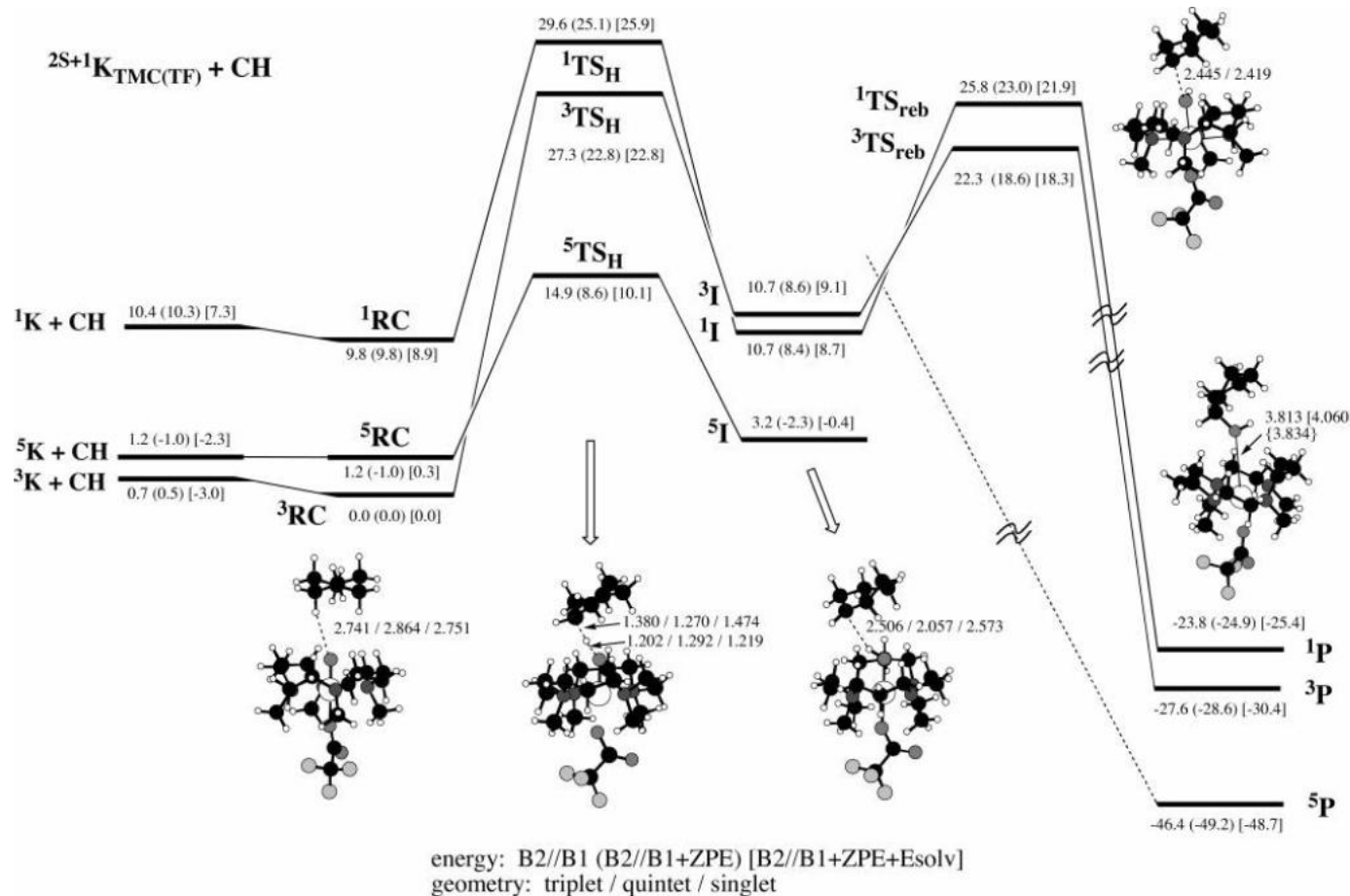^3TS_H
29.4

^3I_H
22.0

$S = 1$
0.0
^3R
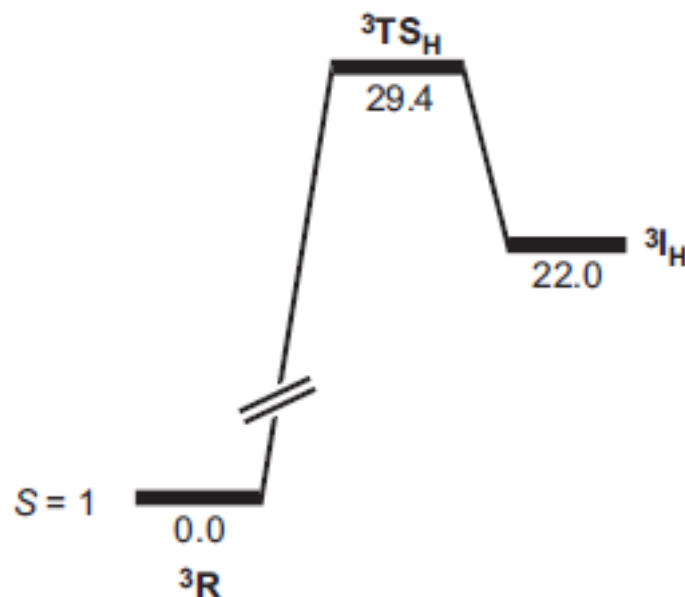
ΔE(Q-T) is so large that the quintet state could not be accessed in Ru case.

Ru^{IV}=O shows the reactivity which simply follows its electrophilicity.
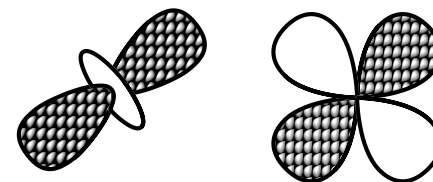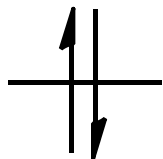
3. Summary and Perspective

Summary

energy: B2//B1 (B2//B1+ZPE) [B2//B1+ZPE+Esolv]
geometry: triplet / quintet / singlet

With the development of computational method and concept of TSR, reactivity and its trend can be somewhat explained.

Summary

Perspective

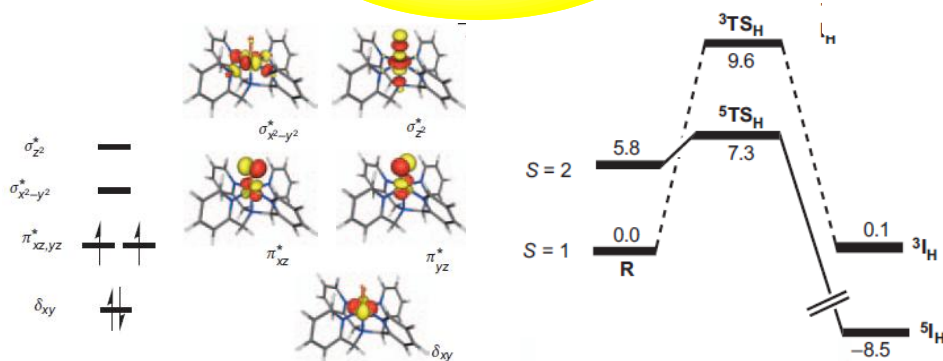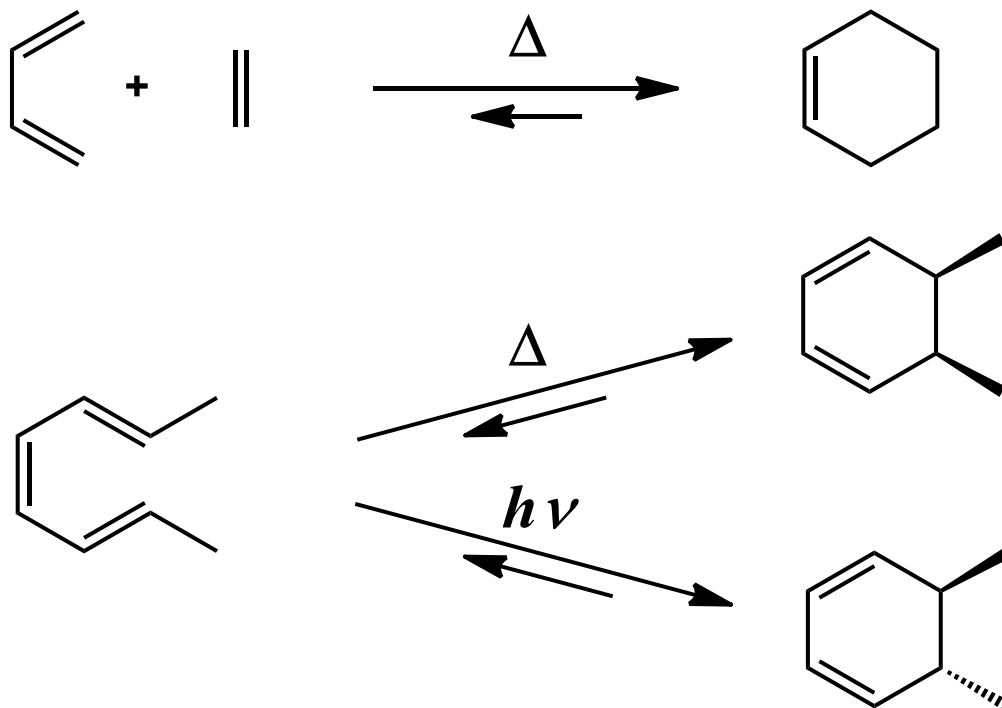## Digressing from the TSR subject...

Pericyclic reaction

Mechanism of these reaction could not be explained and had been named "no-mechanism reaction" until 1960's

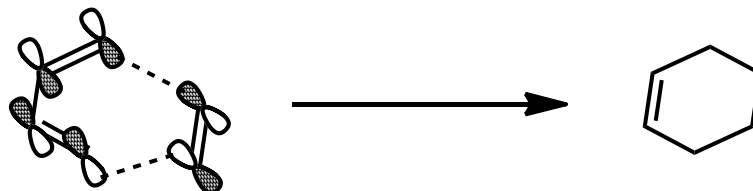# <u>Perspective</u>

K. Fukui   **R. B.Woodward**   **R. Hoffmann**

In the middle of 1960's,

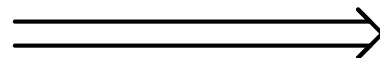**K. Fukui explained the mechanism with *Frontier Orbital Theory*.**

R. B. Woodward, and R. Hoffmann explained the mechanism in the point of
symmetry of molecular orital(*Woodward-Hoffmann rules*).

The Nobel Prize in Chemistry 1981 was awarded jointly to Kenichi Fukui and Roald Hoffmann *"for their theories, developed independently, concerning the course of chemical reactions"*
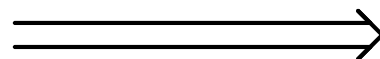
Perspective

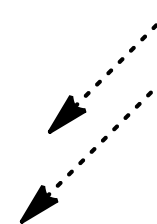**Frontier Orbital Theory
Woodwar-Hoffmann rules** $\longrightarrow$ **Pericyclic Reaction**

**TSR
Spin Chemistry** $\longrightarrow$ **Reactivity of Metals**

**Rational Catalyst
Design on Paper??**

Perspective

However, there are many difficulties...

- Necessity of Computational Method make it difficult for organic chemists
to apply TSR and Spin chemistry to their work.

- Now, those concepts are applied only to explain experimental results.